

Evaluation of Storage Effects on Commercial, Biodegradable, Synthetic or Bio-sourced Hydraulic Fluid

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ABSTRACT

Bio-mass petroleum products are a reality. The U.S. Army has been involved in the development of biodegradable hydraulic products since the 1990s concentrating on industrial type hydraulic fluid, but will bio-based hydraulic fluids be able to stand the test of time? Executive Order 13101¹ endorses the use of bio-mass materials, to reduce dependence on natural resources, utilize renewable resources, and create a new outlet(s) for agricultural products. Even though military equipment is exempt from this executive order, the Fuels and Lubricants Technology Team (FLTT) is being responsive so that military equipment can utilize such a product without a sacrifice in performance.

This paper identifies the chemical and physical properties exhibited by bio-based hydraulic fluids before and after four to five years in storage. It is expected that the bio-based hydraulic fluids will show signs of oxidation and degradation as a result of long-term storage. The test results demonstrated that bio-based hydraulic fluids, as formulated, are not stable and degrade over time.

INTRODUCTION

The U.S. Army is committed to developing new technologies to reduce the environmental impact of the products it uses. Executive Order 13101: "Greening of the Government", is the proposal to make the U.S. Government more environmentally friendly. In an effort to become more environmentally conscious, the Army evaluated bio-based hydraulic fluids for use in combat and tactical equipment.

In 2001, testing was performed at the U.S. Army Tank Automotive Research, Development, and Engineering Center (TARDEC) FLTT laboratory and the TARDEC Fuels and Lubricants Research Facility (TFLRF) located at Southwest Research Institute (SwRI) to determine if commercially available, bio-degradable, bio-based hydraulic fluids could meet or exceed the performance requirements for military combat and tactical hydraulic

fluid specifications², MIL-PRF-46170³ and MIL-PRF-6083⁴. MIL-PRF-46170 is a rust inhibited, fire resistant, synthetic hydrocarbon based hydraulic fluid intended for use in recoil mechanisms and hydraulic systems of military ground vehicles and equipment. MIL-PRF-46170 is the Army's normal-high temperature fluid and has excellent lubricity and stability as well as good fire resistance properties. MIL-PRF-46170 is considered a Class II biodegradable product as defined by the United States Air Force. A Class II biodegradable product must degrade 40% in 28 days and 60% in 84 days⁵. Alternatively, MIL-PRF-6083 is a petroleum based hydraulic fluid used for preservation and operation. It has excellent low temperature properties compared to MIL-PRF-46170 and moderate lubricity; however, it is flammable and not readily biodegradable like MIL-PRF-46170.

The TARDEC study in 2001 was planned for three phases:

- Phase I: Commercial Products Market Survey/Laboratory Screening
- Phase II: In-Depth Laboratory Evaluation
- Phase III: Field Evaluation/Demonstration

In Phase I, none of the fluids met the current specification requirements. The fluids exhibited poor low temperature properties and high acidity. Upon the conclusion of Phase I, the manufacturers were provided the test results and allowed to reformulate their products. There were no restrictions on the reformulations. Phase II evaluated the manufacturers reformulated products. The data generated in Phase II was similar to the Phase I data. The samples had poor low temperature properties and high acid numbers. The reformulations were not successful and still did not meet the military performance specifications. After Phase II was completed, the results of both Phase I and Phase II indicated that bio-based hydraulic fluids, as formulated, could not meet the requirements for the current Army hydraulic fluids. Therefore, Phase III was not conducted due to the inability of the products to meet all of the specification requirements of MIL-PRF-46170 or MIL-PRF-6083.

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For more information regarding the initial evaluation and determination of the commercially, available biodegradable, bio-based hydraulic fluid, please reference SAE Technical Paper 2005-01-1803, *Evaluation of Commercial, Biodegradable, Synthetic or Biosourced Hydraulic Fluid for Use in Military Combat/Tactical Vehicles*².

In 2005, FLTT began follow-up research on the commercially available, biodegradable, bio-based samples previously tested in 2001. This paper will evaluate the bio-based hydraulic fluids to determine if any significant physical or chemical property changes occurred as a result of long-term storage (total of five years from receipt of samples).

SCOPE OF THE EVALUATION

In 2005 and 2006, FLTT conducted a laboratory investigation to determine the long-term storage effects on the commercially available biodegradable, bio-based hydraulic fluids that had initially failed to meet the performance specification requirements for MIL-PRF-6083 and MIL-PRF-46170⁵.

In total, 23 hydraulic fluid samples, each containing a minimum of 25 percent, renewable, bio-source, base-stock were tested. However, the exact amount of bio-material and the complete formulation of the hydraulic fluids were not disclosed to FLTT.

The 23 samples were manufactured by 11 different fluid companies and were stored for a total of four years. The samples were stored in Nalgene® polypropylene bottles in a laboratory where the temperature was controlled; however, the relative humidity was not. The samples were not disturbed or opened during the storage period.

Laboratory data on the fluids was collected per test procedures published by the American Society for Testing and Materials (ASTM) and the Federal Test Method (FTM) 791. Initial testing (2001) of the 23 hydraulic fluids measured the following properties:

- Kinematic Viscosity⁶ @ -40°C, 40°C, and 100°C (ASTM D 445)
- Flash and Fire Point⁷ (ASTM D 92)
- Lubricity (4-Ball Wear)⁸ (ASTM D 4172)
- Total Acid Number (TAN)⁹ (ASTM D 664)
- Water Content by Karl Fischer Coulometric Titration¹⁰ (ASTM D 6304)
- Bimetallic Corrosion¹¹ (ASTM D 6547)
- Low Temperature Stability¹² (FTM 791 M 3458)
- Pour Point¹³ (ASTM D 97)
- Rust Protection (Humidity Cabinet)¹⁴ (ASTM D 1748)

The evaluation performed in 2005/2006 included the same test methods, with the exception of the Rust

Protection test (ASTM D 1748). The Rust Protection test was not conducted due to the limited sample size available for testing.

Additionally, in the four/five years between testing, the laboratory acquired several new pieces of equipment. Therefore, it is important to indicate that the 2005 data collected on Pour Point, Water Content, TAN, and the 4-Ball wear scars were obtained using different test equipment.

With the push for a greener environment and the use of renewable products, many companies are investigating/manufacturing bio-based lubricants. However, the long-term stability of the bio-based hydraulic fluids is unknown, especially for military ground equipment. In general, military ground equipment requires annual hydraulic fluid changes. However, hydraulic fluid could remain in the reservoir of a system for 36 months. Therefore, it is imperative to determine the general trends in the bio-based hydraulic fluid stability. FLTT anticipates chemical/physical property changes in total acid number and water content, which would indicate oxidation and degradation of the bio-based hydraulic fluids.

Additionally, the long-term storage effects on the bio-based hydraulic fluids were thought to be similar to changes experienced with the bio-material in biodiesel. FLTT has completed work, which indicates that the bio-material is not stable and easily oxidizes¹⁵. Furthermore, the acid number of the biodiesels increased rapidly. Based on this previous work with biodiesel, FLTT expected the significant changes to be apparent in the Total Acid Number (TAN) and Water Content of the bio-based hydraulic fluids.

TEST RESULTS AND DISCUSSION

Kinematic Viscosity (ASTM D 445)

Viscosity is an important characteristic of hydraulic fluids. Viscosity is defined as the measurement of a fluids resistance to flow under gravity; therefore, as the temperature of a hydraulic fluid is decreased, its viscosity increases¹⁶.

This method tests a hydraulic fluids resistance to flow under gravity at -40°C, 40°C, and 100°C which is performed in accordance with ASTM D 445, Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids⁶.

Viscosity at -40°C

Table 1 provides a comparison of the viscosity at -40°C data from TARDEC in 2001 and the data from 2005. Test data provided below represents an average of duplicate tests from a single sample.

Table 1 shows that 10 out of the 23 samples showed negligible change in the -40°C viscosity. Six out of the 23 samples remained too viscous to measure and therefore a change could not be determined. Since ASTM does not provide reproducibility data for kinematic viscosity at -40°C; the highest allowable deviation for reproducibility for the types of products listed in ASTM D 445 was used to determine the most significance changes⁶.

However, samples C, M, P, Q, R, T, and W (highlighted in yellow) had unusually high changes in viscosity. The measured viscosity difference at -40°C for these samples are larger than can be attributed by the use of different technicians and lab equipment between 2001 and 2005. The samples showed a decrease in low temperature viscosity. This decrease is counter-intuitive because the products were expected to deteriorate somewhat (i.e. a viscosity increase) or at best, not change at all. Subsequent investigations shall be conducted to better understand the viscosity properties of degraded/degrading bio-based fluids.

SAMPLE ID	2001	2005	% Change
A	TVTM	TVTM	
B	TVTM	TVTM	
C	8529	7592	-11
D	TVTM	TVTM	
E	720	679	-6
F	1687	1770	5
G	TVTM	TVTM	
H	35009	36335	4
I	15107	14871	-2
J	4212	4461	6
K	TVTM	TVTM	
L	TVTM	TVTM	
M	3811	3052	-20
N	3039	2940	-3
O	4075	4042	-1
P	7060	4953	-30
Q	7575	4670	-38
R	4085	2122	-48
S	2299	2253	-2
T	2877	1787	-38
U	2426	2330	-4
V	2269	2213	-2
W	6479	5802	-11

TVTM=too viscous to measure

Figure 1 is a graph of the percent change between 2001 and 2005 data. The graph depicts significant changes for a majority of the samples tested.

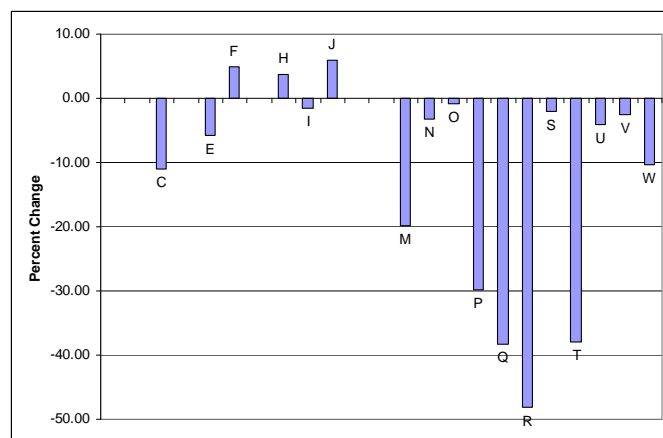


Figure 1. Viscosity @ -40°C

Viscosity at 40°C

Table 2 provides the results for viscosity measured at 40°C from TARDEC in 2001 and the data from 2005. Test data provided below represents an average of duplicate tests from a single sample.

SAMPLE ID	2001	2005	% Change
A	65.20	65.62	0.6
B	46.17	46.97	1.7
C	26.46	25.97	-1.9
D	31.75	32.02	0.9
E	9.37	9.42	0.5
F	16.78	17.27	2.9
G	45.06	45.37	0.7
H	24.60	24.81	0.9
I	41.92	42.15	0.5
J	19.35	19.44	0.5
K	26.94	26.84	-0.4
L	17.19	17.21	0.1
M	17.42	17.47	0.3
N	19.11	19.27	0.8
O	17.33	17.33	0.0
P	20.42	20.46	0.2
Q	22.65	26.58	28.7
R	14.61	14.68	0.5
S	14.24	14.31	0.5
T	13.23	13.23	0.0
U	17.77	17.96	1.1
V	13.69	13.83	1.0
W	24.84	21.87	-12.0

As shown in the table, the 40°C viscosity data remained relatively consistent. However, ten of the 23 (highlighted in yellow) samples showed changes greater than ASTM reproducibility and beyond what can be expected from different equipment and technicians⁶. Samples Q and W

experienced the largest percent change and showed significant signs of deterioration.

Figure 2 is a graph of the percent change between 2001 and 2005 data.

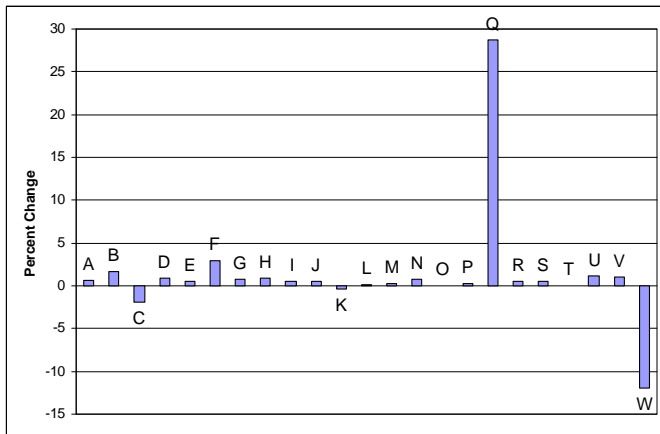


Figure 2. Viscosity @ 40°C

Viscosity at 100°C

Table 3 provides the results for viscosity measured at 100°C from TARDEC in 2001 and 2005. Test data provided below represents an average of duplicate tests from a single sample.

SAMPLE ID	2001	2005	% Change
A	13.36	13.67	2.3
B	9.76	9.90	1.4
C	5.47	5.46	-0.2
D	7.40	7.71	4.2
E	2.84	2.85	0.4
F	4.46	4.60	3.1
G	7.90	7.94	0.5
H	8.29	8.40	1.3
I	5.35	5.32	-0.6
J	5.08	5.15	1.4
K	5.69	5.72	0.5
L	4.12	4.18	1.5
M	4.19	4.19	0.0
N	4.51	4.54	0.7
O	4.09	4.14	1.2
P	13.36	13.67	2.3
Q	4.47	4.47	0.0
R	6.33	6.14	-3.0
S	3.81	3.83	0.5
T	3.63	3.65	0.6
U	3.57	3.57	0.0
V	4.78	4.85	1.5
W	3.49	3.51	0.6

Eleven of the 23 samples tested (highlighted in yellow) exhibited changes greater than the reproducibility allowed by ASTM⁶. The increased viscosities may be an indication of oxidation particles in the sample hindering its ability to flow, or the degradation of a viscosity improver (VI), if formulated into the product.

Figure 3 is a graph of the percent change between 2001 and 2005 data. The graph illustrates a significant change in the bio-based hydraulic fluids.

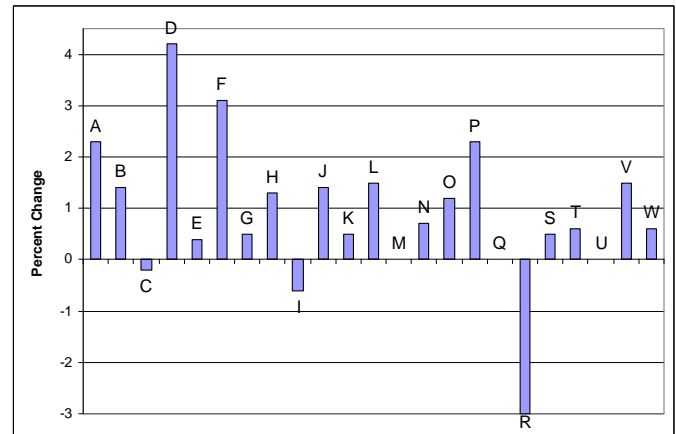


Figure 3. Viscosity @ 100°C

Flash/Fire Point (ASTM D 92)

The bio-based hydraulic fluids were tested in accordance with ASTM D 92, Standard Test Method for Flash and Fire Points by Cleveland Open Cup. The open cup method is a requirement for military tactical/combat hydraulic fluids.

The flash point of a fluid is defined as the minimum temperature at which enough liquid is vaporized to create a vapor mixture that will instantaneously burn when exposed to a flame.

The fire point of a fluid is defined as the minimum temperature at which enough liquid is continuously generated to vapor to burn for five seconds.

Fire resistance is an important safety related property of a hydraulic fluid and is affected by a number of factors including flash point and fire point. Hydraulic fluids are required to operate at extreme pressures in hydraulic systems. High pressure will cause fluid from a ruptured line to spray a great volume of fluid, creating a potential fire hazard¹⁶.

Flash Point

Table 4 provides a comparison of the flash point data from TARDEC in 2001 and the data from 2005. Test data provided below represents an average of duplicate tests from a single sample. Five of the 23 samples (highlighted in yellow) produced results that did not meet reproducibility criteria established by ASTM⁷.

Table 4 - Flash Point (°C)			
SAMPLE ID	2001	2005	Δ Change
A	263	249	-14
B	321	287	-34
C	227	185	-42
D	205	200	-5
E	166	171	5
F	158	162	4
G	291	279	-12
H	269	248	-21
I	252	259	7
J	233	227	-6
K	240	222	-18
L	224	218	-6
M	230	226	-4
N	202	198	-4
O	252	235	-17
P	272	264	-8
Q	237	215	-22
R	222	213	-9
S	226	218	-8
T	216	210	-6
U	204	200	-4
V	177	180	3
W	186	174	-12

Figure 4 visually depicts the delta change between the data collected in 2001 from that collected in 2005. Positive values indicate increase in the flash points while negative values show a decrease. Samples B, C, H, K, and Q exhibited significant changes and possible formation of other lower molecular weight products as part of the deterioration process. Therefore, the decreased flash point showed changes occurred in these samples during the long-term storage and has decreased their fire resistance properties¹⁷.

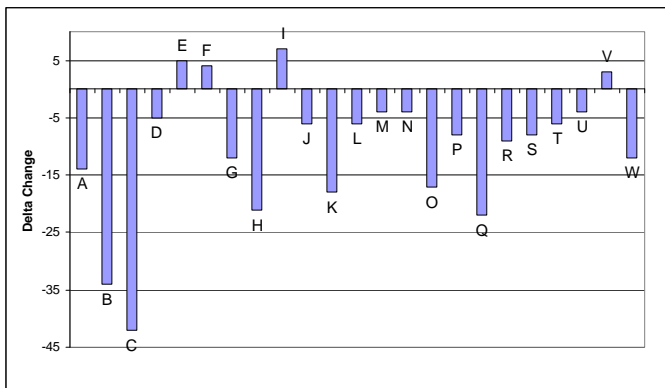


Figure 4. Flash Point

Fire Point

Table 5 provides the results for the fire point data from TARDEC in 2001 and the data from 2005. The table shows that between 2001 and 2005, unlike the flash point data, the fire point data is quite consistent. Sample H is the only sample to exceed the reproducibility criteria established by ASTM⁷ and exhibit a significant change in fire point (highlighted in yellow).

Table 5 - Fire Point (°C)			
SAMPLE ID	2001	2005	Δ Change
A	283	278	-5
B	349	337	-12
C	274	285	11
D	230	227	-3
E	180	176	-4
F	161	168	+8
G	324	326	+2
H	302	285	-17
I	288	299	11
J	238	237	-1
K	257	254	-3
L	255	256	1
M	258	256	-2
N	222	214	-8
O	263	260	-3
P	294	292	-2
Q	252	249	-3
R	243	240	-3
S	245	246	1
T	238	234	-4
U	234	236	2
V	191	192	1
W	262	264	2

Figure 5 provides a graph of the delta changes for the fire point data. In general, the graph shows a decreasing trend in fire points, similar to flash points. However, only sample H changed significantly.

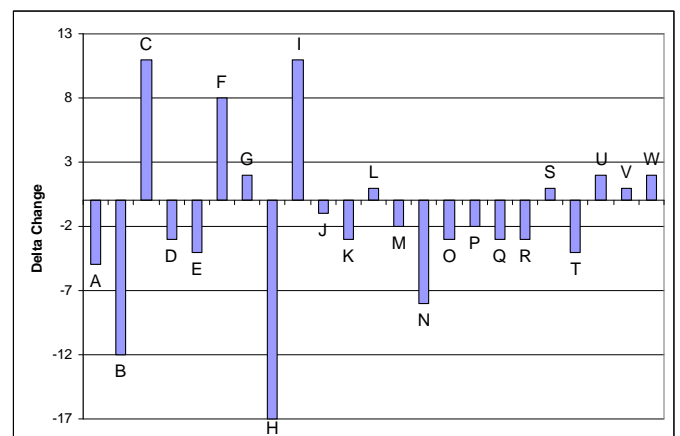


Figure 5. Fire Point

It is worthy to note, sample B had large decrease in fire point (even though the results were within the reproducibility of the test method), similar to the decrease in flash point.

Lubricity (4 Ball Wear) (ASTM D 4172)

ASTM D 4172, Standard Test Method for Wear Preventive Characteristics of Lubricating Fluid (Four-Ball Method) was used to determine the relative wear preventative properties of hydraulic fluids.

Wear within a vehicle's hydraulic system, cannot be completely eliminated; only reduced. Two complementary methods can be used to reduce wear; mechanical and lubrication. The mechanical aspect depends on the pressure, temperature, speed, and materials used. Anti-wear additives that are incorporated into the fluids enhance hydraulic fluid lubrication¹⁸. MIL-PRF-46170 and MIL-PRF-6083 prescribe the following test conditions: 1200 rpm, 40 kg load, test temperature of 75°C, and a test time of 60 minutes^{3,4}.

Table 6 provides the results of the lubricity data from SwRI and FLTT in 2001 and the data from 2005.

Table 6 - Lubricity (Four-Ball) (mm)			
SAMPLE ID	2001	2005	Δ Change
A	0.42	0.35	-0.07
B	0.40	0.42	+0.02
C	0.65	0.53	-0.12
D	0.40	0.37	-0.03
E	0.35	0.43	+0.08
F	0.43	0.52	+0.09
G	0.44	0.56	+0.12
H	0.43	0.40	-0.03
I	0.45	0.38	-0.07
J	0.43	0.65	+0.22
K	0.47	0.49	+0.02
L	0.89	0.84	-0.05
M	0.93	0.81	-0.12
N	0.43	0.59	+0.16
O	0.48	0.49	+0.01
P	0.50	0.45	-0.05
Q	0.53	0.41	-0.12
R	0.43	0.38	-0.05
S	0.39	0.37	-0.02
T	0.36	0.39	+0.03
U	0.39	0.44	+0.05
V	0.40	0.37	-0.03
W	0.53	0.60	+0.07

Please note that the method used to measure wear scars changed. In 2001, a Scherr Tumico optical comparator was used. The comparator calculates the wear scar based on three points in the shape of a triangle. In 2005, the wear scar was measured using the

Falex Digital Scar Measurement System. This equipment calculates the wear scar using the diameter across the x- (horizontal) and y- (vertical) axis of the wear scar.

The four ball wears scars were within the reproducibility criteria established by ASTM⁸. Therefore, the anti-wear additives did not show deterioration during storage and the lubricity of the bio-based hydraulic fluids were not negatively affected.

Total Acid Number (TAN) (ASTM D 664)

To determine the acidity of the hydraulic fluids one can use ASTM D 664, Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration. The TAN of a fluid is measured in milligrams of base required to neutralize all acidic components of the fluid.

The data collected in 2001 was performed manually. The 2006 data was generated using a Mettler Toledo DL55 automatic titrator. The automatic titrator results were verified against results generated using the manual titrations. The results were well within the repeatability limits established by ASTM⁹. Therefore, the 2006 results reported below were generated using the automatic titrator

Table 7 provides the results for the TAN data from TARDEC in 2001 and the data from FLTT in 2006.

Table 7 - Total Acid Number (TAN) (mg KOH/g)			
SAMPLE ID	2001	2006	% Change
A	0.91	2.36	159.3%
B	1.34	1.42	6%
C	0.34	0.17	-50%
D	0.53	0.62	17%
E	0.22	0.34	54.5%
F	0.55	0.78	41.8%
G	0.51	0.53	3.9%
H	0.38	0.45	18.4%
I	0.49	0.36	-36.3%
J	0.75	0.76	1.3%
K	1.83	6.64	262.8%
L	0.38	1.69	344.7%
M	0.25	1.74	596%
N	0.73	0.32	-56.2%
O	1.09	2.46	125.7%
P	1.09	2.38	118.3%
Q	0.22	0.38	72.7%
R	0.41	0.97	136.6%
S	0.40	0.97	142.5%
T	0.38	0.87	128.9%
U	1.67	1.70	1.8%
V	0.17	0.43	152.9%
W	0.25	0.32	28%

Figure 6 compares the TANs between 2001 and 2006. The samples with a positive value indicate an increase in acid number while negative values showed a decrease.

Six samples (B, C, G, I, J, and U) indicated that acid formation was not present after storage. Eleven of the 23 samples did not meet the reproducibility criteria established by ASTM and indicated significant changes in the samples. Ten samples showed an increase in acid value while one showed a decrease larger than the (highlighted in yellow above). Typically, an increase in the acid value indicates the expected deterioration but a decrease beyond the test reproducibility was not expected.

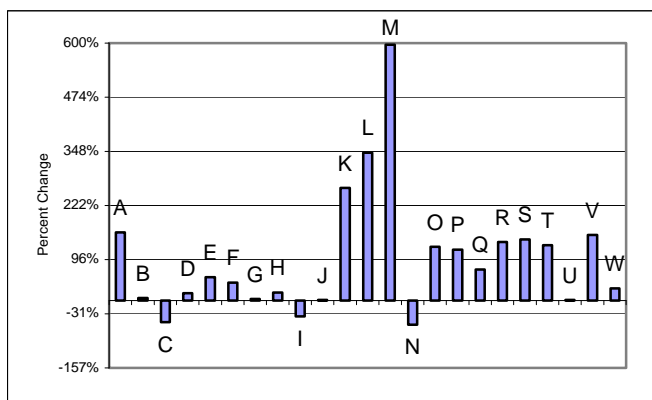


Figure 6. Total Acid Number (TAN)

The degradation of the bio-based hydraulic fluids cannot be compared across the board. The degradation experienced in the bio-based hydraulic fluids is directly influenced by the type of basestock, the amount of basestock used in the formulation, how the products were manufactured, and the additive packages blended to the fluids. Unfortunately, this information was not made available to FLTT. Therefore, only comments on the general trend of bio-based products can be made. Bio-based materials oxidize over time, which results in an increase in TAN.

Water Content (ASTM D 6304)

Coulometric Karl Fischer Titration for water content was conducted in accordance with ASTM D 6304, Standard Test Method for Determination of Water in Petroleum Products, Lubricating Oils, and Additives. The water content, measured in mass percent (%), can lead to premature corrosion and wear within a hydraulic system¹⁰. The titration was performed with iodine because one mole of iodine reacts with one mole of water and therefore can give an accurate amount of water in any given sample.

Table 8 provides the results of the water content data from TARDEC in 2001 and the data from FLTT in 2005.

However, FLTT procured a new Karl Fischer water titrator in 2003. But FLTT continued to use the same reagents, cathode, and anode solutions in the new water titrator.

SAMPLE ID	2001	2005	Δ Change
A	0.044	0.026	-0.018
B	0.038	0.034	-0.004
C	0.079	0.121	0.042
D	0.040	0.034	-0.006
E	0.010	0.008	-0.002
F	0.068	0.042	-0.026
G	0.038	0.027	-0.011
H	0.094	0.112	0.018
I	0.100	0.106	0.006
J	0.038	0.080	0.042
K	0.035	0.039	0.004
L	0.092	0.036	-0.056
M	0.070	0.046	-0.024
N	0.054	0.040	-0.014
O	0.080	0.035	-0.045
P	0.098	0.032	-0.066
Q	0.012	0.009	-0.003
R	0.115	0.080	-0.035
S	0.097	0.075	-0.022
T	0.068	0.068	0.000
U	0.061	0.067	0.006
V	0.045	0.036	-0.009
W	0.152	0.164	0.012

Figure 7 shows the delta change of the total water content between 2001 and 2005. The water content data proved to be the most interesting data collected. Bio-based materials tend to be hydrophilic (water attracting) and thus an increased water content over time is expected. However, more than half of the samples tested (15 samples) had a significant decrease in water content (approximately 30%). Seven samples had an increase in water content of approximately 14%, while sample T showed no change.

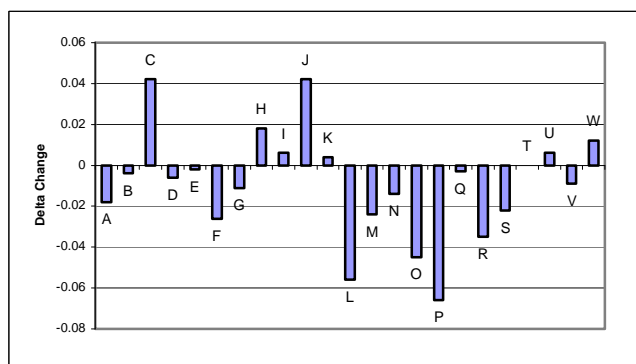


Figure 7. Water Content

The results can be a result of the storage techniques as well as the fact that different coulometric Karl Fisher

titration equipment was used. Although samples were kept in capped bottles, there was no attempt to ensure a complete seal. Additionally, even though the lab environment is temperature controlled, it does not effectively control humidity.

Bimetallic Corrosion (ASTM D 6547)

One of the corrosion tests performed on the bio-based hydraulic fluids was ASTM D 6547, Standard Test Method for Corrosiveness of Lubricating Fluid to Bimetallic Couple (also known as Galvanic Corrosion). Bimetallic corrosion is important because it evaluates the potential for a chemical attack on a metal by any contaminants, water or acid, in the fluid. Galvanic corrosion utilizes two dissimilar metals and an electrolyte (see figure 8).

The bimetallic corrosion test is important because hydraulic systems can be manufactured with dissimilar metals. For this test, the disk, acting as the less noble metal, becomes the anode. In a corrosion cell, the anode undergoes an oxidation reaction (loss of electrons), while the cathode undergoes a reduction reaction (gain of electrons). Therefore, the disk loses electrons while the clip (more noble metal) gains electrons¹⁹. The hydraulic fluid acts as the electrolyte, passing the ions between the metals. Since the disk loses the electrons, it shows the signs of corrosion, etching, pitting, and/or discoloration.

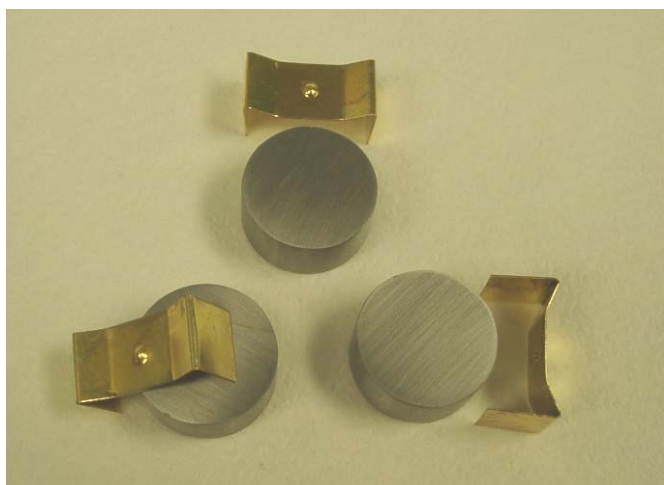


Figure 8. Bimetallic Corrosion Metals

Table 9 provides the results for the bimetallic corrosion from FLTT in 2001 and 2005/2006. In Phase 1 of the initial evaluation conducted in 2001, nine of the samples were not tested due to limited lab personnel.

Table 9 - Bimetallic Corrosion		
SAMPLE ID	2001-2002	2005/2006
A	NT	Pass
B	NT	Pass
C	NT	Pass
D	NT	Pass
E	Pass	Pass
F	Pass	Pass
G	NT	Pass
H	NT	Pass
I	NT	Pass
J	Pass	Pass
K	NT	Fail
L	NT	Pass
M	Pass	Pass
N	Pass	Pass
O	Pass	Pass
P	Pass	Pass
Q	Pass	Pass
R	Pass	Pass
S	Pass	Pass
T	Pass	Pass
U	Pass	Pass
V	Pass	Pass
W	Pass	Pass

NT=not tested

The data from Table 9 shows that all of the samples tested passed except sample K (highlighted in yellow). However, 2001 data was not available to determine if this represents a change. Overall, long-term storage did not have a significant impact on the bimetallic corrosion properties of the bio-based hydraulic fluids.

FLTT cannot fully determine the effectiveness of the additive technologies used to prevent corrosion since the Rust Protection (humidity cabinet) test was unable to be conducted on the stored bio-based hydraulic fluids.

Low Temperature Stability (FTM 791 M 3458)

The Low Temperature Stability Test for Oil is performed to gather information pertaining to the effectiveness of the hydraulic fluid in freezing climates. The test is conducted for 72 hours at -40°C and 72 hours at -54°C^{3,4}. Low temperature stability determines whether a fluid can withstand these temperatures without crystallizing, separating, gelling, or completely hardening¹².

Table 10 provides a comparison of the low temperature stability data from FLTT in 2001 and 2005. In Phase I of the initial testing, ten of the samples were not tested at -54°C because they froze solid at -40°C

temperature viscosity bath set at -75°C was used to lower the temperature of the sample being tested.

Table 11 provides a comparison of the pour point data from FLTT in 2001 and 2005-2006.

Table 10 - Low Temperature Stability				
SAMPLE ID	-40°C		-54°C	
	2001-2002	2005	2001-2002	2005
A	Fail	Fail	NT	Fail
B	Fail	Fail	NT	Fail
C	Fail	Fail	NT	Fail
D	Fail	Fail	NT	Fail
E	Fail	Pass	Fail	Fail
F	Pass	Pass	Fail	Fail
G	Fail	Fail	NT	Fail
H	Fail	Fail	NT	Fail
I	Fail	Fail	NT	Fail
J	Fail	Fail	NT	Fail
K	Fail	Fail	Fail	Fail
L	Fail	Fail	NT	Fail
M	Fail	Fail	Fail	Fail
N	Fail	Fail	Fail	Fail
O	Pass	Fail	Fail	Fail
P	Fail	Fail	NT	Fail
Q	Fail	Fail	Fail	Fail
R	Fail	Fail	Fail	Fail
S	Fail	Fail	Fail	Fail
T	Fail	Fail	Fail	Fail
U	Pass	Pass	Fail	Fail
V	Pass	Pass	Fail	Fail
W	Pass	Pass	Fail	Fail

NT=not tested

The data shows that only four samples, F, U, V, and W passed at -40°C in 2001 and 2005 (highlighted in yellow). The data indicates that none of the samples were able to meet the requirements at -54°C in 2001 and 2005.

Low temperature properties are essential for combat/tactical vehicle hydraulic fluids. Army equipment must be able to operate in ALL environmental conditions without having to change the fluids. Test results indicate these fluids would not function in certain operating conditions.

Pour Point (ASTM D 97)

The pour point of a fluid is defined as the lowest temperature at which a fluid is observed to flow¹⁶. The pour points were measured manually in accordance with ASTM D97, Standard Test Method for Pour Point of Petroleum Products. The method was altered slightly due to equipment restrictions in 2005. A low

Table 11 - Pour Point (°C)			
SAMPLE ID	2001-2002	2005-2006	Δ Change
A	-23	-17	+6
B	-21	-11	+10
C	-50	-49	+1
D	-35	-32	+3
E	-43	-48	-5
F	-50	-59	-9
G	-21	-26	-5
H	-44	-44	0
I	-47	-33	+14
J	-43	-44	-1
K	-39	-48	-9
L	-40	-33	+7
M	-43	-49	-6
N	-44	-44	0
O	-45	-50	-5
P	-50	-43	+7
Q	-45	-46	-1
R	-60	-47	+13
S	-66	-53	+13
T	-63	-47	+16
U	-54	-53	+1
V	-66	-53	+13
W	-63	-51	+12

The pour points of the bio-based hydraulic fluids indicate the lowest temperature of its utility for certain applications. 11 out of 23 samples showed a difference in the pour point temperature greater than the reproducibility allowed¹³ (highlighted in yellow). Two samples, F and K, showed a decrease in temperatures exhibiting better pour point than previously tested. The increases can be an indication of the fluid's deterioration.

Figure 8 shows the delta change between the 2001-02 and 2005-06 data.

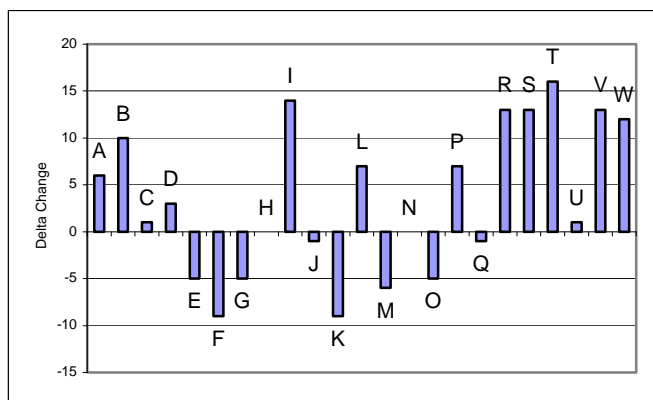


Figure 9. Pour Point

It is unknown whether pour point depressants were used in the fluid formulation or their potential impact during storage

CONCLUSION

Previous evaluations of commercially, available biodegradable, bio-based hydraulic fluids determined that the formulations were not robust enough to meet the current hydraulic fluid performance specifications for Army ground equipment. However, it was important to determine the propensity for the bio-material in the hydraulic fluids to oxidize and degrade. Since the formulations were not disclosed, we cannot generate specific conclusions. Therefore, the evaluation reported here depicts the trends that occurred in the bio-based hydraulic fluids during storage.

23 bio-based hydraulic fluids were evaluated to determine the long term effects of storage. According to the data collected, the following property changes to the fluid were observed:

- The hydraulic fluids did not uniformly change suggesting degradation is formulation dependent
- Viscosity decreased at low temperatures and showed significant changes at high temperatures
- Flash point and fire point showed only minor changes in most samples
- Lubricity was unchanged
- Total acid number significantly changed in over half of the samples indicating the oxidation and degradation of the bio-material
- Water content decreased or remained unchanged
- Bimetallic corrosion remained unchanged
- Low temperature stability was unchanged; however, most of the samples froze when exposed to low temperatures
- Pour points increased significantly.

Appendix 1 contains a consolidated table demonstrating which physical/chemical properties changed drastically during storage. Additionally, the table highlights the samples that exhibited the most oxidation/degradation.

Sample E was the only sample which did not show any signs of degradation following long-term storage. However, this sample still does not meet the specification requirements to be used in military combat or tactical vehicle hydraulic systems. Ten of the 23 samples (samples B, C, H, K, L, P, Q, R, T, and V) exhibited signs of degradation during four or more test experiences.

Bio-based hydraulic fluids are not ready for use in military combat/tactical equipment. The data presented concludes that the technologies used in these bio-based hydraulic fluids cannot meet the specification requirements for combat/tactical vehicles and the fluids are not suitable for long-term storage as formulated.

Future research and development may yield a more stable bio-based fluid. At such a time, the bio-based hydraulic fluids can be reevaluated for potential use in military/combat vehicles.

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Appendix 1: Long Term Storage Stability Testing

	-40°C Viscosity	40°C Viscosity	100°C Viscosity	Flash Point	Fire Point	4Ball Wear	TAN	Water Content	Galvanic Corrosion	Low Temp Stability @ -40°C*	Pour Point
A			X				X			X	
B		X	X	X						X	X
C	X	X		X						X	
D		X	X							X	
E											
F		X	X								X
G										X	
H		X	X	X	X					X	
I										X	X
J			X							X	
K				X			X		X	X	X
L			X				X			X	X
M	X						X			X	
N		X					X			X	
O			X				X			X	
P	X		X				X			X	X
Q	X	X		X						X	
R	X		X				X			X	X
S							X			X	X
T	X						X			X	X
U		X									
V		X	X				X				X
W	X	X									X

* = Bio-based hydraulic fluids froze to a solid when tested in 2001 and 2005.

X = indicates a property change greater than ASTM reproducibility